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The Role of Ion Transport in the Failure of High Areal Capacity Li Metal Batteries

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ABSTRACT: Recent advancements in electrolyte research have substantially improved the cycle life of Li metal batteries (LMBs) but often under moderate areal capacity. The design principles overwhelmingly emphasize the reduction of electrolyte reactivity toward Li. In this work, we find that high areal capacity (>6 mAh cm⁻²) Lillsulfurized polyacrylonitrile (SPAN) batteries fail primarily due to shorting events when paired with four types of localized high-concentration electrolytes (LHCEs), which is correlated with electrolyte transport properties, including ionic conductivity and Sand's capacity. These LHCE systems, despite their high Coulombic efficiencies for Li metal cycling, produce macroscopically non-uniform Li deposits when operating under transport limitation. This deficiency leads to short circuit over repeated cycling, as evidenced by a quantitative, statistical analysis of SEM images. Based on these insights, we fabricated a 2 Ah pouch cell, which



demonstrates a cell energy density of >260 Wh kg⁻¹ for more than 70 cycles. Our findings emphasize the significance of the bulk transport properties of electrolytes and the statistical morphological information on cycled Li for long-life LMBs.

i-S batteries are being intensively investigated due to their promise of high energy density. Moreover, sulfur is anaturally abundant, an attribute that is more desirable due to the ever-increasing cost of Co and Ni. While much attention has been paid to improving the cycling stability of the sulfur cathode related to the well-known polysulfide shuttling issue, achieving the same for the lithium metal anode in a Li-S battery is also a major challenge in its own right.¹⁻⁴ When Li metal is paired with a 4 V layered oxide cathode (LiTMO₂₁ TM = Ni, Co, Mn), a moderate areal capacity (\sim 3 mAh cm⁻²) is used to ensure long cycle life,⁵⁻¹¹ as it avoids severe morphology degradation and the increased parasitic reactions associated with high capacity and/or high current density cycling.¹²⁻¹⁵ However, this strategy is untenable for cells employing S-based cathodes, which rely on increased cathode loading to compensate for their reduced operating voltage (~2 V).¹⁶

Electrolyte design for the Li metal anode has focused on reducing reactivity and promoting the formation of a stable solid–electrolyte interface (SEI), largely through introducing fluorine to the passivating layer.^{17–22} For example, Yu et al. demonstrated that, by introducing CHF₂ groups onto the solvent molecules, >99.9% CE in half cell and 270 stable cycles in full cell were achieved.²³ Increasing the salt concentration of the electrolyte is another effective method to reduce parasitic reactivity due to the reduced free solvent available for

decomposition, while exposing more fluorinated anions for interphase formation.^{24,25} However, higher salt concentration results in high viscosity, poor wettability, and low ionic conductivity.²⁶ To solve this, introducing a fluorinated, nonsolvating diluent into a concentrated system to form a localized high-concentration electrolyte (LHCE) has been demonstrated to reduce the electrolyte viscosity while maintaining electrochemical stability.^{27–29} These electrolytes retain the contact-ion-pair (CIP) structure present in high-concentration systems, rather than the solvent-separated-ion-pair (SSIP) solvation structures commonly observed in dilute electrolyte solutions.^{5,11,27,28,30,31} However, CIP structures tend to produce a substantial reduction in ion conductivity due to reduced ionicity of the solution.

Ionic conductivity and other transport properties such as transference number also play important roles in determining lithium's morphology and cycling stability. These metrics can be applied to calculate the Sand's capacity for a given system, which is the total charge passed when the surface

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Figure 1. Physical properties of LHCEs with different main solvents. Radar plots of concentration, ionic conductivity measured with and without separator, viscosities, transference numbers of (A) LDBE, (B) LDiPE, (C) LDEE, and (D) LDME. Sand's capacity of different electrolytes versus current density, calculated based on data (E) without and (F) with separator.

concentration of the lithium ions approaches zero (the time when this occurs is called the Sand's time).³² Applying this metric, Bai et al. demonstrated a distinct shift in plated Li morphology, where a more dendritic morphology was proposed to result from interphasial depletion of $\text{Li}^{+,33}$ A reduction in either ionic conductivity or Li^{+} transference number thus leads to a reduction in Sand's capacity, presenting a significant challenge when applying LHCE systems in highloading Li-S batteries, which may undergo interphasial Li⁺ depletion at the anode when charged.

When dendritic lithium deposition starts due to a combination of reactivity and transport limitation, the morphology of the electrode is very often non-uniform, perhaps due to local interphasial composition, stress, or pressure differences. However, such non-homogenous growth is typically not observed in the electrochemical data (e.g., CE) of LHCE systems due to their intrinsic stability with Li metal. While images of the Li metal anode are often collected using scanning electron microscopy (SEM), very little attention is paid to the macroscopic non-uniformity of the plated morphology. This methodology is particularly problematic when we study the dendrite-related shorting behavior of batteries, which is intrinsically a point failure event that depends on poor regions of plated morphology instead of the commonly referred to "representative images". As a result, it is possible for an electrolyte to produce a very high CE for Li cycling and local dendrite growth at the same time. The



Figure 2. Coulombic efficiencies and morphologies of electrochemically deposited Li in different LHCEs prove the compatibility between the employed electrolytes and Li metal. (A) Voltage profiles of the Coulombic efficiency measurement using the method proposed by Adams et al.³⁹ (B) SEM images of electrochemically deposited Li in different electrolytes.

dendrite growth will lead to short circuit, particularly at high loading and/or current.

In this work, we show that, for electrolytes which should produce comparable cycling performance due to high CE values for Li cycling, disparate transport properties determine their failure rate from dendritic growth. This tendency manifests itself as the growth of local dendritic structures that lead to cell shorting even without any apparent deterioration of average CE. We study four LHCE electrolytes with high areal loading (>6 mAh cm^{-2}) SPAN as the cathode, a material which is known to offer stable cycling free of the polysulfide dissolution mechanism when the appropriate electrolyte is chosen.^{4,16,34–37} Based on the understanding of the role of transport, we identified a DME-based LHCE as the optimal choice to fabricate a 2 Ah pouch cell. Our study illustrates the significance of electrolyte bulk properties and macroscopic uniformity of Li morphology in realizing stable cycling of high-energy-density Li metal batteries with high areal capacity cathodes.

Electrolyte Transport Properties. Four LHCEs, LDBE, LDiPE, LDEE, and LDME, were prepared with different ethers as main solvents due to ether's superior stability with Li metal anode, and BTFE as the diluent. The four ethers are dibutyl ether (DBE), diisopropyl ether (DiPE), diethyl ether (DEE), and dimethoxyethane (DME), respectively. These four electrolytes were saturated with LiFSI salt and then diluted by BTFE in a 1:2 solvent-to-diluent mole ratio.

Figure 1A-D shows the radar plots of physical properties of the different LHCEs, including the concentration, conductivity, viscosity, and transference number. The concentration follows the trend of LDME > LDEE > LDBE > LDiPE. The ionic conductivity measured in Swagelok cells without separator shows the trend of LDME \gg LDEE > LDiPE > LDBE, consistent with the dielectric constants of the four primary solvents. The same conductivity trend persists when measured with separators in coin cells. Lower values were observed in the latter case due to the presence of separators. This reduction in conductivity is similar to recent reports.³⁸ Furthermore, the electrolyte viscosity and transference number were also measured. LDME showed the highest viscosity and lowest transference number. LDiPE is the least viscous and has the highest transference number. The viscosity trend follows the same trend as the concentration.

We also calculated the Sand's capacity using the model proposed by Bai et al.³³ It is determined by the following equation:

$$C_{\text{Sand}} = Jt_{\text{Sand}} = \frac{\pi D_{\text{app}} (Z_{\text{c}} C_0 F)^2}{4J(1 - t_+)^2}$$

where *J* is the current density, D_{app} is the diffusion coefficient, Z_c is the charge number of the cation, C_0 is the bulk concentration, *F* is the Faraday constant, and t_+ is the transference number.



Figure 3. Capacity retentions and voltage profiles of high areal capacity (>6 mAh cm⁻²) LillSPAN cells in different electrolytes. (A) Charge/ discharge areal capacity retention of LillSPAN cells with different electrolytes. (B) Voltage profiles of LillSPAN cells with different electrolytes. Cycle numbers versus Sand's capacity of cells with different electrolytes based on data measured (C) without and (D) with separator. Cells were cycled under C/20 for two cycles, followed by C/5 cycling.

Figure 1E,F shows the Sand's capacities of different electrolytes with respect to the current density, which are calculated based on the conductivity with and without separators, respectively. In both cases, the LDME showed the highest Sand's capacity. This implies that cells with LDME electrolytes are less prone to ion depletion, which is one of the main driving forces for uncontrollable dendrite growth.

Electrolyte Compatibility with Li Metal Anode. CE measurement and morphological analysis of electrochemically deposited Li were performed to test the compatibility between LHCEs and Li metal. LillCu half cells with different electrolytes were tested with the CE measurement protocol proposed by Adams et al.³⁹ Specifically, the testing protocol included the following steps. A charge of 5 mAh cm⁻² was applied to deposit Li at a current density of 0.5 mA cm⁻². The Li was then completely stripped until the electrode potential reached 1 V. This process was used to form a stable SEI. Next, 5 mAh cm^{-2} Li was deposited on Cu. Subsequently, 1 mAh cm⁻² Li stripping and depositing cycles were repeated 10 times. Finally, all Li was stripped until the electrode potential reached 1 V. The CE was calculated by dividing the total stripped capacity by the total deposition capacity after the formation cycle. For all electrolytes evaluated, the cycling capacity of 1 mAh cm⁻² is safely below the Sand's capacity, which ensures our measurement is free from transport limitation (the test condition corresponds to the orange dot marked on Figure 1E,F). As shown in Figure 2A, LillCu cells exhibit similarly high CE (~99%) in different electrolytes. Li plated in different electrolytes was also investigated by SEM, where dendrite-free morphologies were found on samples prepared with all four LHCEs (Figure 2B). The above results prove that these four types of LHCEs are all highly compatible with Li metal anode. We should note that the vast majority of lithium metal cycling efficiency values reported in the literature were obtained under similar conditions when the transport limitation was not triggered.^{5,27,40,41}

Electrolyte Performance in High Areal Capacity Lill SPAN Full Cells. Our previous report has shown that, to deliver >300 Wh kg⁻¹ energy density at the cell level, SPAN cathodes with >6 mAh cm⁻² areal capacity are needed.¹⁶ Figure 3A shows the cycling performance of four electrolytes in full cell configuration when >6 mAh cm⁻² SPAN cathodes were paired with Li metal. The charge and discharge current density is 1.2 mA cm⁻² for all cells. Cells with LDBE, LDiPE, and LDEE electrolytes failed at the 23rd, 27th, and 46th cycles, respectively, while the cell with LDME electrolyte lasted 130



Figure 4. Morphology of Li cycled in LDEE and LDME, showomg macroscopic inhomogeneity. (A) Optical image of cycled Li and separator harvested from the LDEE cell. (B) Low-magnification SEM image of the Li anode cycled in the LDEE cell. (C) High-magnification SEM image of the mossy Li region in panel B. (D) High-magnification SEM image of the compact Li region in panel B. (E) Optical image of cycled Li and separator harvested from the LDME cell. (F) Low-magnification SEM image of the Li anode cycled in the LDME cell. (G) High-magnification SEM image of the porous Li region in panel F. (H) High-magnification SEM image of the compact Li region in panel F.

cycles without noticeable capacity fading. A symptom of cell failure is classic soft shorting behavior. The charging capacity exceeded the theoretical value as Li dendrites penetrated the separator, leading to electron leakage. The voltage fluctuated as the Li dendrites propagated to the cathode and broke after reacting with the positive electrode (Figure 3B). Additionally, it is worth noting that cells with LDiPE and LDEE electrolytes experienced only minimal capacity fade before shorting, which implies that the cell failure is not due to continuous impedance growth as a result of an increase in SEI/CEI thickness or cathode disintegration; rather, it is due to the onset of an internal short circuit. One potential complication is the influence of the high-loading SPAN cathode on lithium metal behavior. SPAN is known to swell during the first cycle. To examine whether the electrolytes have any effect on the degree of swelling, we imaged the SPAN electrodes cycled in LDEE and LDME. Figure S1 shows the cross-sectional

images of pristine and discharged SPAN cathodes. Similar swelling behavior, i.e., expansions of 29.2% and 27.2%, respectively, was observed in electrodes harvested from cells with LDEE and LDME electrolytes. The similar levels of swelling indicate that any minor differences in cathodes are unlikely to be responsible for their differences in cell failure.

We now correlate the electrolyte transport properties with the cell shorting behavior. We notice that the onset of shorting started earlier for electrolytes with lower conductivities rather than with lower CE values. Figure 3C,D illustrates the correlation between cycle number and Sand's capacity, where monotonically increasing relationships are observed. Testing conditions for the full cells are marked in Figure 1E,F. When considering the effect of the separator, it is clear that the cells are all cycled in conditions that exceed the Sand's capacity to varying degrees. This provides a theoretical explanation for the dendrite shorting behavior. In systems with low Sand's



Figure 5. Statistical analysis of collected SEM images, quantying the macroscopic non-uniformity. Particle size distribution of Li grains from the high-magnification SEM images of cycled Li harvested from cells with (A) LDEE and (B) LDME. Particle segmentation result of low-magnification SEM images of Li cycled in (C) LDEE and (D) LDME. Plots of bottom 25% particles in terms of grain size from (E) panel C and (F) panel D and their index of dispersion.

capacities, ion depletion can be triggered when paired with a high-capacity cathode, which will accelerate dendrite growth. The other electrolyte properties, including the viscosity and transference number, show no apparent correlation with the shorting behavior. LDME shows the highest viscosity and lowest transference number but the longest cycle life among the four electrolytes studied. LDiPE is the least viscous and has the highest transference number but delivered only 27 cycles before shorting.

To further verify the causality mentioned above, we reduced the conductivity of the LDME electrolyte by further dilution and tested the cyclability of the LillSPAN full cell. Specifically, an electrolyte named LDME2 was prepared by decreasing the solvent to diluent ratio from 1:2 to 1:7, resulting in the ionic conductivity dropping from 9.33 to 2.87 mS cm⁻¹ (Figure S2). The cycling performance of a LillSPAN cell with a cathode areal capacity of 7.1 mAh cm⁻² is shown in Figure S3, which developed soft shorting behavior in its 42nd cycle. We altered the dendrite shorting behavior without changing the electrolyte chemistry by manipulating the ionic conductivity, which further proves the significance of electrolyte transport properties. We also note that adding more diluent has previously been shown to increase lithium cycling efficiency by promoting the formation of CIP solvation structures.⁴²

Morphological Analysis of the Cycled Li-Macroscopic Uniformity. More than the electrolyte property itself, Li morphology is directly responsible for the cell's short circuit. We disassembled the cells with the LDEE and LDME electrolytes to compare their morphologies. Figure 4A,E shows the optical images of the Li and separators harvested from the cycled cells. There is a clear difference between the two Li electrodes in macroscopic uniformity. The relatively darker regions on the optical image correspond to porous and mossy Li morphology, while the silver-colored regions are compact and flat Li deposits. The Li cycled in LDEE showed agglomeration of the porous Li, while the high aspect ratio Li on LDME sample is uniformly distributed. The black dots in the optical image of the separator serve as additional evidence for the existence of dendrite shorting in the LDEE cell. Figure 4B,F shows the low-magnification SEM images of the cycled Li, where noticeable uniformity differences were observed. In Figure 4B, orange and red circles correspond to the porous and dense Li deposition, respectively, which are also shown in Figure 4C,D. Similar morphology segregation was observed on Li cycled in LDME, but it is much more spatially uniform



Figure 6. LillSPAN pouch cell using a high areal capacity SPAN cathode (\sim 8 mAh cm⁻²) with the lean (3 g Ah⁻¹) LDME electrolyte delivers high energy density. (A) Energy density retention of the pouch cell. (B) Voltage profile of the pouch cell. (C) Optical image of the pouch cell.

(Figure 4F). There is no chunky aggregation of dendritic Li or compact Li. Instead, a uniform mixture of two kinds of Li morphology was observed (Figure 4G,H). Similar observations were also found on the Li cycled in LDME2 electrolyte, where spatial non-uniformity was self-evident (Figure S4). The above results demonstrate the significance of the macroscopic uniformity of the Li morphology in the cycle life of Li metal batteries.

To quantify the morphological differences that we observed in the SEM images, we performed particle segmentation analysis using the Avizo software.43 The particle size distributions of Li grains cycled in different electrolytes are shown in Figure 5A,B, where the data was collected from the measurements on 18 SEM images to provide statistical information (Figures S5 and S6). The average size of the Li grains on the LDEE sample is larger than that on the LDME, 17.73 μ m² compared to 13.50 μ m². It is generally accepted that a larger Li grain size is preferred due to reduced parasitic reactions and improved reversibility during stripping. This observation agrees with the Li CE measurement, where the LDEE electrolyte delivered higher efficiency than LDME. However, the Li cycled in LDEE also showed a larger standard deviation in particle size, which is associated with the shorting behavior. The larger average size but wider distribution means the coexistence of more dendritic and chunky Li at the same time. The abundance of Li dendrites will result in a higher probability of internal short circuits. In addition to particle size, the spatial distributions of different Li features were studied. The low-magnification SEM images in Figure 4B,F were processed, with the results shown in Figure 5C,D, where the Li

particles are segmented and colored. The bottom 25% Li particle in size was extracted and replotted in Figure 5E,F. A clear difference in the dendritic Li distribution was observed. A parameter termed index of dispersion (ID) was used to evaluate the spatial uniformity of the dendrites.⁴⁴ (See Experimental Details in the Supporting Information for details.) A much higher ID was found on the LDEE sample, indicating a much more non-uniform distribution of Li dendrites (98.86 compared to 16.52). The top 25% Li particle in size was also extracted, as shown in Figure S7, where a higher ID was found on the LDEE sample (4.41 compared to 1.12). By analyzing the SEM images, we concluded that a narrow particle size distribution and a uniform spatial distribution of Li dendrites are essential for long-life high areal capacity LillSPAN cells because they mitigate the danger of internal shorting.

LillSPAN Pouch Cell Demonstration. To demonstrate the superiority of the LDME electrolyte in practical applications, we fabricated a 2 Ah LillSPAN pouch cell. Specifics of the cell design are provided in Table S1, which features a lean electrolyte amount of 3 g Ah⁻¹ and a high cathode areal capacity of ~8 mAh cm⁻². Figure 6A shows the energy density versus the cycle number. The LillSPAN pouch cell delivered >260 Wh kg⁻¹ in energy density with minimal degradation for over 70 cycles. The voltage profiles shown in Figure 6B indicate that the cell delivered exceptionally high areal (~8 mAh cm⁻²) and gravimetric specific (>700 mAh g⁻¹) capacity without significant polarization. The capacity retention and Coulombic efficiency data are shown in Figure S8. The optical image in Figure 6C shows the dimensions of the pouch cell (22 cm^2 electrode area). In Table S2, we compared our pouch cell data with the state-of-art LillSPAN cells in the literature. The comparison clearly shows the merit of our pouch cell, as it realizes high areal capacity, lean electrolyte, and low N/P ratio at the same time in a high-capacity pouch cell. Despite the challenging lean electrolyte condition, the high energy density pouch cell confirms the benefits of using electrolytes with improved transport property in high-capacity LMBs.

In conclusion, we designed four types of LHCEs with different main solvents in order to examine the effect of bulk transport properties on cell performance when high areal capacity cycling is involved. These cycling conditions often exceed the Sand's capacity and trigger dendritic lithium growth in these otherwise highly stable, high CE electrolytes. Short circuit happened in cells with high CE LHCEs, except for the LDME. The longevity of the LillSPAN cells was correlated with the electrolyte transport properties, including the ionic conductivity, Sand's time, and capacity. Further studies on the morphology of cycled Li revealed significant macroscopic uniformity differences, which were then quantified by image processing techniques. A wider distribution of Li grain size and spatial aggregation of dendritic Li were found on the Li cycled in the shorted LDEE cell while absent in the LDME cell. Leveraging the benefits of the more conductive LDME electrolyte, we designed and assembled a 2 Ah LillSPAN pouch cell, which delivered >260 Wh kg⁻¹ energy density at the cell level. Our work provides a distinctive perspective on designing electrolytes for high areal capacity and high energy density Li metal batteries. We advocate for the further development of high CE efficiency with high ion conductivities in order to mitigate transport-driven dendrite growth when cycled at high areal capacities. Finally, macroscopic uniformity of the lithium anode is essential in order to mitigate the tendency of cell shorting.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c01114.

Experimental methods, SEM images of SPAN cathode and Li metal anode, physical properties of electrolytes, performance of cells with LDME2, Li particle distribution, pouch cell information. (PDF)

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Author Contributions

P.L., H.L., and Z.W. conceived the idea. Z.W. performed the electrochemical experiments, SEM characterizations, electrochemical characterization, viscosity measurement, and image analysis. H.L. prepared the electrolyte. H.K. wrote the MATLAB algorithm to analyze the particle distribution. J.H. participated in the discussion, including the correlation with Sand's capacity. C.A., L.S., D.P.L., D.L., C.N., and J.X. fabricated the pouch cell. Z.W., H.L., P.L., and J.H. wrote the manuscript. All authors provided input.

Notes

The authors declare no competing financial interest.

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